# ELECTROCHEMICAL OXIDATION OF ALBERTA COALS IN NEW ENVIRONMENTS

by

Dr. I. Birss

Department of Chemistry
The University of Calgary
2500 University Drive N.W.
Calgary, Alberta T2N 1N4

LEGISLATURE LIBRARY
DEC -7 1992
EDMONTON

FINAL REPORT

to

ALBERTA ENERGY AND NATURAL RESOURCES
OFFICE OF COAL RESEARCH AND TECHNOLOGY

February 10, 1990

CONFIDENTIAL

A/CERRF Proj. 2835-R6-87/1
Date Received July 5, 1991
Copy to file ☑ Research Manager ☐
Library ☐ E M & R. Ottawa ☐

## EXECUTIVE SUMMARY

The electrochemical oxidation of four types of Alberta coals has been accomplished by the electrolysis of concentrated acetic acid/sulfuric acid mixtures, using $Fe^{3+}$ ions as the redox mediator. Low yields of $CO_2$ have been correlated with high yields of liquid products and high reaction rates for long periods of time. The activity of the coals in this medium is Coal Valley > Highvale > Vesta > Bow City. The liquid products appear to be primarily low molecular weight (< ca. 165) alcohols and carboxylic acids. Coal Valley coal (60 mesh) has also shown substantial extents of liquefaction in slurries composed of sulfuric acid mixed with either propionic acid or DMSO, as well as in alkaline solutions using a $Co^{2+/3+}$ mediator. Finally, a new kinetic approach has been developed in order to more accurately establish the coal oxidation rate constants and which has enhanced our understanding of the mechanism of this reaction.

**ABSTRACT**

The electrochemical oxidation of four Alberta coals of different rank and particle size has been carried out in a range of aqueous and mixed aqueous/non-aqueous environments at 90°C. This has been achieved with the use of transition metal mediators ($Fe^{2+/3+}$ and $Ir^{2+/3+}$) which are oxidized at a Pt electrode at a controlled potential, and which in turn, oxidize the coal in the slurry. Our previous data, obtained in sulfuric acid environments, has now been more rigorously treated, using a new kinetic model. This has led to the establishment of more accurate and meaningful rate constants and has increased our understanding of the basic mechanism of the reaction of coal with transition metal ions in these types of experiments.

Alberta coals have also been oxidized in organic acid media, with the goal of enhancing the extent of coal liquefaction at the expense of the production of gases such as $CO_2$. Also, high rates of liquefaction are correlated with the retention of high levels of coal activity for long periods of time of oxidation. The best results to date have been obtained in acetic acid and in propionic acid slurries, to which sulfuric acid has been added. Although only some of these liquid products could be analyzed, the yields of products such as alcohols and short-chain carboxylic acids are relatively high. Coal oxidation in DMSO/sulfuric acid media, as well as in pH 11 environments, also appears to be very promising in terms of the yield of liquid products.

## 1. INTRODUCTION

The environmental concerns about the present-day utilization of coal have created substantial interest in developing new technologies based on the use of coal as a source of energy. Also, the decrease in global oil reserves has been instrumental in the search for new methods to generate liquid hydrocarbons from coal and other solid fossil fuels. Electrochemical coal conversion has the potential to be one of the most environmentally safe methods of this kind.

The electrolysis of acidic coal slurries was first reported in 1979. Since these first reports [1-3], several research groups have shown that, when certain transition metal ions are used as electron transfer mediators in sulfuric acid solutions, coal can be readily oxidized to CO and $CO_2$, while hydrogen can be produced at high rates at the cathode [4-11]. Some evidence for the formation of liquid products has also been reported.

The overall process can be represented by reactions (1) and (2), using $Fe^{3+}$ as the example of the transition metal ion mediator, while m, n, p, q, r and s are coefficients of unknown value, but which depend on the experimental conditions, and $Coal_{ox}$ depicts the oxidized products which remain attached to the coal surface.

At the anode:

$$Fe^{2+} \xrightarrow{k_e} Fe^{3+} + e^- \quad (E^{o\prime} = 0.771 \text{ V vs. SHE}) \qquad (1a)$$

At the cathode:

$$H^+ + e^- \longrightarrow 1/2\ H \qquad (1b)$$

In the slurry:

$$Fe^{3+} + mCoal + nH_2O \xrightarrow{k_c} Fe^{2+} + [pCoal_{ox} + qCO_2 + rCO + \text{other products}] + sH^+ \qquad (2)$$

Here, $k_c$ is the chemical rate constant for reaction (1) and $k_e$ is the mass transfer rate constate (rate of transport of $Fe^{2+}$ to the electrode), respectively.

The advantages of electrochemical coal slurry oxidation include the production of clean, sulfur-free carbonaceous products, as well as hydrogen, the latter at ca. half the cell voltage which is normally required to produce oxygen and hydrogen via the electrolysis of water. However, one reported drawback to this approach has been that with time of electrolysis, the coal surface gradually becomes covered with oxidized functional groups, resulting in a lowering in the rate of oxidation with time, and a consequent inability to fully oxidize the coal particles [5,7-16]. Also, a substantial fraction of the products formed in the typical sulfuric acid medium is $CO_2$, generally viewed as a relatively undesireable product.

In our efforts to overcome these limitations, we had carried out some preliminary experiments [14] which had shown that the electrolysis of coal slurries in Fe-containing acetic acid solutions resulted in a significantly higher proportion of dissolved

(liquid) hydrocarbon products and diminished $CO_2$ yields, as compared to the case in sulfuric acid slurries. Also, it was indicated that the electrochemical activity remained higher for longer periods of time [14], indicative of less build-up of surface products with time of electrolysis. These results have prompted a portion of the present study, i.e. the investigation of coal slurry oxidation in various new (different from sulfuric acid) slurries to achieve the maximize the extent of coal liquefaction.

Therefore, the specific goals of the present study were to conduct a thorough study of the electrochemical oxidation of various types of Alberta coals of different particle sizes in Fe-containing acetic acid slurries to determine the activity of the coal towards oxidation and the nature of the products obtained. In addition, an investigation of the feasibility of electrochemically oxidizing selected Alberta coals in a number of other new environments, such as other organic acid slurries, in mixed aqueous and non-aqueous solvents, and in mildly alkaline (pH ca. 11) slurries, was undertaken. Finally, new redox mediators were to be sought in these studies.

It is also important that, in the initial phase of this work, it was recognized that the kinetic approach, used to obtain rate constants for Alberta coal oxidation in sulfuric acid slurries, and reported previously [14], was incomplete. Therefore, in the present research period, this kinetic model and data treatment was refined, leading to the establishment of more accurate rate

constants and a better overall understanding of the reaction between coal and the redox mediator.

## 2.0 EXPERIMENTAL METHODOLOGY

### 2.1 General Experimental Approach

The general procedure utilized in this research involved the addition of 6 grams of a particular pre-treated Alberta coal sample to 120 mL of 1M $H_2SO_4$ to which known amounts (15 mM) of a redox mediator, such as $Fe^{2+}$, had been added. At a constant temperature, stirring rate and electrode potential, the current was monitored as a function of time. The analysis of the gaseous products was carried out as a function of time of electrolysis, and solution-soluble liquid products were determined after the completion of each experiment.

### 2.2 Electrochemical Set-up

The electrochemical experiments were carried out using the equipment referred to previously [14]. A three-compartment cell was employed (Fig. 1), with each compartment containing one of the three electrodes. The details of the cell operation and justification for its design were presented earlier [14].

A large area high purity Pt foil (Aldrich, 7 $cm^2$, 99.99%) was used as the working electrode (WE), the anode, during the electrolysis experiments, while a larger area Pt gauze electrode and a reversible hydrogen electrode (RHE) or a saturated calomel electrode (SCE) were used as the counter (CE) and reference (RE)

electrodes, respectively. In all cases, the WE was cleaned by repeated cycling of its potential between that for the oxygen evolution (OER) and the hydrogen evolution (HER) reactions before each experiment.

In all of the experiments, the solution was continuously deaerated by bubbling high purity argon gas through the solution at a controlled rate. The coal slurry was stirred at a reproducible rate during each experiment using a large Teflon-coated stir bar driven by a magnetic stirrer. This was done in order to keep the coal particles in suspension and also as stirring is required to control the rate of mass transport of the redox mediator to the WE surface.

### 2.3 Solvents and Chemicals

AristraR grade sulfuric acid (BDH) was used together with triply distilled water to make up the sulfuric acid solutions. Analytical grade $FeSO_4$ $7H_2O$ was used as the source of ferrous ions. Acetic acid, phosphoric acid, iridium hexachloride (Aldrich), cobalt (II) chloride, 2,2'-bipyridine (Sigman), chloroform, benzene and other organic solvents were also all of analytical grade.

The coal samples were obtained from the Department of Coal and Hydrocarbon Processing of the Alberta Research Council. Their origin, rank and particle sizes are given in Table 1.

## 2.4 Pre-treatment of Coal

Coal samples were subjected to a careful pre-treatment process before using them in the electrolysis experiments. The principal steps involved in the process are shown in Fig. 2. This was done in order to leach out all of the inorganic matter from the coal, and in particular, any Fe-containing species, so that it could be certain that a controlled quantity (added later) of the redox species would be present during the electrochemical experiments. Also, the pre-treatment was carried out in order to achieve a reproducible chemical and physical condition of the coal.

Approximately 200 grams of coal were agitated in 2 litres of 1M sulfuric acid at 25$^{o}$C for ca. 24 hours. This sample was then filtered and again subjected to the same washing process. The sample was then refluxed (95 to 97$^{o}$C) in about 2 litres of 1M sulfuric acid for ca. 24 hours, cooled and then filtered. Then it was refluxed again in 1M sulfuric acid for another 24 hours, cooled and filtered. The coal sample was then washed free of acid by repeated agitation in triply distilled water, filtered and dried ;under vacuum over anhydrous $CaSO_4$ at room temperature. The coal which was not used immediately in an electrochemical experiment was stored in a refrigerator.

## 2.5 Product Analysis

### 2.5.1 Gaseous Product Analysis

The gaseous products obtained from the anode compartment

during electrolysis were analyzed with a Shimadzu 8A gas chromatography (GC) and a Shimadzu C-R1B chromatopac integrator. A Carbosieve SII column was used for the analysis. The gaseous products were flushed out of the cell with argon gas and were collected continuously in a gas collecting tube. Samples were periodically withdrawn and injected into the GC. After each sampling, the remaining gas in the tube was removed in order to ensure the collection of fresh gas from the cell for the next analysis. The total amount of gaseous products, i.e. primarily $CO_2$ and CO, produced during an experiment, could be determined from the periodic GC analysis of the contents of the collecting tube and the measured total volume of gas released from the cell in the experiment.

**2.5.2** Liquid Product Analysis

The liquid products obtained from acidic coal slurry electrolysis were analyzed after the competion of the relevent experiments. The liquid products were extracted from the aqueous acid medium into suitable organic solvents using liquid-liquid extraction procedures. The principal steps involved in the extraction process are given in Fig. 3. Once extracted, the organic compounds were dissolved in 10 mL of either chlorform, benzene, or methylene chloride. This solutions was then analyzed using GC and GC-MS techniques. An HP 5890A GC, fitted with a Megabore column (DB1-15M, 0.53 mm ID) and a model VG 7070F MS, coupled with a Shimadzu 91 GC, were employed.

## 3. RESULTS AND DISCUSSION

### 3.1. *General Approach to the Determination of Coal Activity*

The electrochemical oxidation of pre-treated Alberta coals was initially carried out by controlled potential electrolysis (CPE) at 1.0 V *vs.* RHE in a $H_2SO_4$ slurry containing known amounts of added $FeSO_4$. The rate of oxidation of the coal in the slurry could be established from the analysis of the current *vs.* time response (I/t) during the electrolysis [11,15-17].

A typical set of I/t data collected from an experiment in which 6 grams of Vesta coal was oxidized in 120 ml of 1M $H_2SO_4$ containing 15 mM of $FeSO_4$ at 90°C and 1.0 V *vs.* RHE is plotted in Figure 4 (curve a). As seen in the figure, the current decreases fairly rapidly at short times but then decreases more slowly at longer times of electrolysis. This decay of the current with time, as compared to the theoretical response, which would be seen if the coal had completely regenerated $Fe^{2+}$ by reaction (1) (Fig. 4, curve b), has been reported previously in the literature and has been attributed to the build-up of oxidized organic functionalities at the coal surface with time of electrolysis [5-9,11,13]. This results in a gradual diminishment of the rate of reaction (1).

It should be noted that the absolute value of the oxidation current at any time depends on the coal:iron ratio in the slurry [14,15]. In the present study, a relatively small ratio (3.3 mg of coal per ml of solution per mM of $Fe^{2+}$) was selected in most cases so that the loss of activity could be observed within

convenient times (24 hours) of electrolysis.

The I/t plots obtained in the electrolysis experiments can be processed to obtain the rate constant for the electrochemical oxidation of coal by a given redox mediator. Numerous analyses of the kinetics of the electrochemical coal oxidation reaction have been made [7-11,19-21], although no common agreement regarding the best mode of treatment of the experimental data to obtain the kinetic parameters and the data interpretation (to determine the mechanism of electrochemical coal oxidation) has been reached.

The first attempt to analyze the kinetics and the mechanism of coal slurry oxidation was made by Dhooge *et al* [7,8]. In their work, a pseudo-first order reaction (w.r.t. $Fe^{3+}$) was assumed for the oxidation of sub-bituminous coal by $Fe^{3+}$ ions. They obtained a rate constant for the electrochemical oxidation of coal by assuming steady-state catalytic current conditions after *ca.* 10 hours of electrolysis of a coal slurry (175 g/ml) in the presence of 1 mM $Fe^{2+}$. A rate constant of $2.6 \times 10^{-5}$ $s^{-1}$ was obtained at 20°C for the oxidation of San Juan coal. However, the determination of the rate constant of the oxidation of coal using this approach may not be valid, since steady-state current conditions are not generally observed [5,11,14,15] at any time of electrolysis, unless the concentration of the coal is in large excess to that of $Fe^{3+}$, as in references 7 and 8.

Anthony and Linge [9] attempted to determine the rate of electrochemical oxidation of coal by the potentiometric titration

of coal with acidified $Fe^{3+}$ solutions. They found the rate of coal oxidation to be independent of the $Fe^{3+}$ and $Fe^{2+}$ concentrations in the slurry at all times and the rate of coal oxidation to be proportional to $t^{-1/2}$, indicating a mass transport controlled reaction. Anthony and Linge had difficulty in reconciling this diffusion model with the polymeric, porous, and macromolecular nature of coal and did not report a rate constant. Nevertheless, they concluded that the rate of coal oxidation depends solely on the concentration of active sites on the coal particle surfaces, that different sites on the coal surface may react at different rates and that numerous reactions (with different rate constants) could be observed at once.

A rigorous kinetic treatment was presented by Kreysa *et al* [11]. They assumed second order reaction kinetics (first order in each of $Fe^{3+}$ and coal) and considered both the forward and reverse rate of reaction (1). However, in the analysis of their data to obtain the coal reaction rate as a function of time, a maximum in the rate at *ca*. 80 minutes of reaction (Fig. 7 of reference 11) was obtained. We have reanalyzed their data to understand the origin of this maximum, but were unable to obtain it. The consequence of the presence of a maximum in the coal oxidation rate at *ca*. 80 minutes in reference [11] is that the reverse rate constant for reaction (1) obtained by a curve fitting method, was by necessity, greater than the forward rate constant. However, this is unreasonable as this would suggest that oxidized coal exposed to a $Fe^{2+}$/ 1M $H_2SO_4$ solution would

oxidize $Fe^{2+}$ at open circuit potential (OCP) conditions. In fact, it is known that under OCP conditions, coal is oxidized by $Fe^{3+}$ in 1M $H_2SO_4$, as in reaction (1).

Two other kinetic analyses of coal slurry oxidation have been published more recently [20,21]. Similar to Anthony and Linge [9], Kawakami *et al* [20] suggest the simultaneous occurrence of many different reactions during coal oxidation by $Fe^{3+}$ and that different functional groups react and disappear at different rates. In their kinetic analysis, they have assumed an infinite number of rate constants and have used curve-fitting methods to simulate their data on this basis. Although a reasonable match of the data has been obtained by this method, it is our view that this model, with so many variables, has no physical meaning. In their studies with the oxidation of Illinois No. 6 (high volatile C bituminous) coal, Kawakami *et al* [20] reported two rate constants, each representing different extents of oxidation. It is important to note that the kinetic model of Kawakami *et al* [20] is also based on the assumption of competitive adsorption of $Fe^{2+}$ and $Fe^{3+}$ on the coal surface. If this assumption is correct, a loss of $Fe^{2+/3+}$ from the slurry due to their adsorption on the coal surface should be observed. It will be shown in our work that this is not the case. It is also noteworthy that the rate constants reported by Kawakami *et al* [20] also incorporate the rate constant of the oxidation of pyrite which leaches into the slurry during the electrolysis.

Lalvani [21] has suggested the existence of a different

rate-controlling step in the oxidation of coal by $Fe^{3+}$ in acidic slurries. The essence of the treatment presented by Lalvani [21] is the assumption that coal oxidation is limited by the rate of diffusion of the oxidant ($Fe^{3+}$) to the coal particle surface and the rate of reaction is then determined by the thickness of the diffusion layer around the coal particles. Such a model is difficult to visulize when considering the porous, irregular nature of the coal particles and, in fact, Anthony and Linge [9] have completely rejected such a model. Lalvani's treatment [21] predicts an observed constant current with time of electrolysis. However, such behavior has never been reported in the literature [1-5,7-11,13,14,15].

Because of the inadequacies of the previously reported kinetic methods discussed above, we have developed a modified approach during this reporting period to analyze the kinetics of electrochemical coal oxidation by $Fe^{3+}$ in acidic slurries. The coal oxidation reaction can be visualized as a reaction between surface active sites such as hydroxyl, phenolic, carboxylic, acyl, etc. groups and $Fe^{3+}$ as suggested in the literature [1-4,6,8-10,12,13]. The slow step in the overall process is presumed to be the interaction of these two reactants during the electron transfer process, similar to the model proposed by Kreysa *et al* [11], and hence a second order reaction is assumed. The overall kinetic treatment is most similar to that of Kreysa *et al* [11], except that we have assumed an irreversible reaction.

## 3.2. The Kinetic Model - A New Approach

### 3.2.1. *Electrochemical Oxidation of Coal Slurries*

The electrochemical oxidation of coal mediated by $Fe^{3+}$ in acidic slurries is usually carried out under potentiostatic conditions at an applied potential of 1.0 V *vs.* RHE [5,7,8,11,13,14-16,20,21]. Under these conditions, the current as reaction (2) proceeds is measured as a function of electrolysis time. The current contains information about the total concentration of $Fe^{2+}$ ($C_R$) in the slurry as well as its rate of consumption at the electrode, $\left(\frac{dC_R}{dt}\right)_{ecl}$ [11,22], as in equations (3) and (4).

$$I_t = nFAk_e(C_R)_t \tag{3}$$

$$I_t = -nFV\left(\frac{dC_R}{dt}\right)_{ecl,t} \tag{4}$$

where $I_t$ is the measured current for reaction (2), A is the area of the electrode, V is the volume of the slurry, F is the Faraday constant and n = 1 for the $Fe^{2+/3+}$ redox couple. In equation (4), the subscript ecl indicates that this change in $C_R$ is brought about solely by the electrochemical oxidation of $Fe^{2+}$ at the electrode, and the negative sign is consistent with the decrease in the $Fe^{2+}$ concentration at potentials at which oxidation (+) currents are tracked.

Under typical experimental conditions, when reactions (1) and (2) occur simultaneously, the overall flux of $Fe^{2+}$ at time, t, $\left(\frac{dC_R}{dt}\right)_{Total,t}$, in the coal slurry depends both on the rate of coal oxidation (generation of $Fe^{2+}$) $\left(\frac{dC_R}{dt}\right)_{coal,t}$, and the rate of

electrochemical oxidation of $Fe^{2+}$ (consumption of $Fe^{2+}$) at the anode, $\left(\frac{dC_R}{dt}\right)_{ecl,t}$, and can be expressed as,

$$\left(\frac{dC_R}{dt}\right)_{Total,t} = \left(\frac{dC_R}{dt}\right)_{coal,t} + \left(\frac{dC_R}{dt}\right)_{ecl,t} \qquad (5)$$

The rate of generation of $Fe^{2+}$ is determined by the rate of reaction (1), while $Fe^{2+}$ is consumed at different rates at the electrode, depending on its concentration and $k_e$. Differentiating equation (3) w.r.t. time and rearranging, we obtain;

$$\left(\frac{dC_R}{dt}\right)_{Total,t} = \frac{1}{nFAk_e}\left(\frac{dI}{dt}\right)_t \qquad (6)$$

for the overall flux in the concentration of $Fe^{2+}$. From equation (4), we obtain the rate of consumption of $Fe^{2+}$ at the electrode at 1.0 V under potentiostatic conditions,

$$\left(\frac{dC_R}{dt}\right)_{ecl,t} = -\frac{1}{nFV} I_t \qquad (7)$$

Substituting (6) and (7) into equation (5) and rearranging, leads to equation (8).

$$\left(\frac{dC_R}{dt}\right)_{coal,t} = \frac{1}{nFAk_e}\left(\frac{dI}{dt}\right)_t + \frac{1}{nFV} I_t \qquad (8)$$

Equation (8) is a global equation which can describe any electrocatalytic process similar to that represented by reactions (1) and (2). In this particular case, it can be used to calculate the rate of oxidation of coal by $Fe^{3+}$, as suggested by Kreysa *et al* [11].

Assuming second order kinetics, the rate of oxidation of coal (reaction (1)) can also be expressed as,

$$\left(\frac{dC_R}{dt}\right)_{coal,t} = k_C Co_t C_{coal,t} \quad (9)$$

where Co is the total concentration of $Fe^{3+}$ in the slurry. The concentration of coal at time, t, $C_{coal,t}$, is very difficult to estimate due to the heterogeneous and variable nature of coal surfaces. But $C_{coal,t}$ can be expressed as follows,

$$C_{coal,t} - C_{coal,o} - C_{coal,r,t} \quad (10)$$

where $C_{coal,o}$ represents the initial concentration of active sites before the commencement of electrochemical oxidation, while $C_{coal,r,t}$ represents the concentration of sites reacted after time, t. The charge, $Q_t$, passed after time, t, of electrolysis is directly related to $C_{coal,r,t}$. However, $Q_t$ also contains the charge equivalent to the $Fe^{3+}$ concentration present in the at time, t, i.e. $nFV(C_{R,o} - C_{R,t})$. Therefore,

$$Q_t = nFV(C_{R,o} - C_{R,t}) + zFV\, C_{coal,r,t} \quad (11)$$

The value of z (the number of electrons involved in the complete oxidation of each active site on the coal surface) is difficult to estimate. Depending on the oxidation state of the carbon atom in the reacting functional group of the active site, z can vary from 1 to 8. Kreysa *et al* [11] have used a value of 2 for z as per the mechanism of coal oxidation suggested in their paper. However, the exact value of z is unknown, and hence we have assumed z = 1 for ease of calculation.

Equation (11) can be rearranged as,

$$C_{coal,r,t} = \frac{Q_t}{zFV} - \frac{1}{z}(C_{R,o} - C_{R,t}). \quad (12)$$

Substituting equation (12) into equation (10),

$$C_{coal,t} - C_{coal,o} = \frac{Q_t}{zFV} + \frac{1}{z}(C_{R,o} - C_{R,t}). \quad (13)$$

Substituting (13) into equation (9) we obtain;

$$\left(\frac{dC_R}{dt}\right)_{coal,t} = k_C Co_t\left[C_{coal,o} - \frac{Q_t}{zFV} + \frac{1}{z}(C_{R,o} - C_{R,t})\right] \quad (14)$$

As $(C_{R,o} - C_{R,t}) = Co_{,t} = \frac{1}{k_e FA}(I_o - I_t)$, and substituting it into equation (14), leads to equation (15).

$$\left(\frac{dC_R}{dt}\right)_{coal,t} = k_C \frac{(I_o - I_t)}{k_e FA}\left[C_{coal,o} - \frac{Q_t}{zFV} + \frac{1}{zFk_e}(I_o - I_t)\right] \quad (15)$$

Equating (8) and (15) and rearranging, leads to equation (16).

$$\frac{1}{(I_o - I_t)}\left[\left(\frac{dI}{dt}\right)_t + \frac{k_e A}{V} I_t\right] = k_C C_{coal,o} - \frac{k_C}{zFA}\left[Q_t - \frac{V}{Ak_e}(I_o - I_t)\right] \quad (16)$$

Equation (16) permits the determination of the rate constant, $k_C$, of the coal oxidation reaction. A plot of $\frac{1}{(I_o - I_t)}\left[\left(\frac{dI}{dt}\right)_t + \frac{Ak_e}{V} I_t\right]$ *vs.* $\left[Q_t - \frac{V}{Ak_e}(I_o - I_t)\right]$ should give straight line plots with a slope of $\frac{k_C}{zFA}$. Equation (16) also allows the calculation of the initial concentration of active coal sites, $C_{coal,o}$, from the y-intercept of the plots.

Various experiments were designed to test the concept of reversibility of reaction (1) as was proposed by Kreysa *et al* [11]. In one experiment, the electrochemical oxidation of coal was carried out for *ca.* 24 hours and then the cell was kept at OCP conditions for *ca.* 64 hours. The $Fe^{3+}$ concentration was then measured using voltammetric methods. If any appreciable degree

of reversibility had been present, the solution should have contained some $Fe^{3+}$ ions. The absence of $Fe^{3+}$ in the slurry, as shown in Fig. 5 after *ca.* 64 hours at OCP conditions, clearly demonstrates the absence of reverse reaction.

In another electrolysis experiment, small aliquots of a concentrated $Fe^{3+}$ solution were added to a slurry containing 15 mM of total Fe concentration after ca. 24 hours of electrolysis. An immediate increase in the current was observed, as shown in Fig. 6. Since the I/t response reflects the rate of the coal oxidation reaction, the increase in current observed with the sudden increase in $Fe^{3+}$ concentration indicates the strong dependence of the reaction rate on the $Fe^{3+}$ concentration.

### 3.3. Electrochemical Oxidation in Acetic Acid Media

#### 3.3.1. *General Electrochemical Activity*

A detailed investigation of the electrochemical oxidation of four types of Alberta coals (two particle sizes) was carried out in 10 M acetic (HOAc) + 3 M $H_2SO_4$, with $Fe^{3+}$ as the mediator at 90°C at an applied potential of 1.0 V vs. RHE.

In Fig. 7, the I/t response obtained from a long time (24 hours) electrolysis of 6 grams of Vesta (200 mesh) coal in 10 M HOAc + 3 M $H_2SO_4$ slurry containing 15 mM $FeSO_4$ is shown (curve a) along with the I/t response (curve b) for the oxidation of 15 mM $FeSO_4$ under identical conditions but without any coal added. As seen in the figure, the current for the oxidation of coal in 10 M HOAc + 3 M $H_2SO_4$ slurry remains high for a long period of time as

compared to the 1M $H_2SO_4$ slurry (Fig. 4). The enhancement of the activity of coal towards oxidationmay be attributed to the higher solubility of organic products in this medium vs. that in either acid alone. The higher rate constant obtained in this medium as opposed to that in $H_2SO_4$ is also indicative of the prevention of the deactivation of the surface of the coal particles during the electrochemical oxidation.

It should be pointed out that, although the magnitude of the current for the initial oxidation of $Fe^{2+}$, $I_o$, was less in 10 M HOAc + 3 M $H_2SO_4$ slurries than in 1 M $H_2SO_4$ slurries, this difference in the $I_o$ values is not a reflection of diminished or altered rates of reaction. Rather, it is caused only by the difference in the magnitude of the diffusion coefficients of $Fe^{2+}$ in these two media.

### 3.3.2. *Kinetic Analysis*

The rate constant of electrochemical oxidation of various coals in the acetic acid media was determined by analyzing the I/t response according to equation (16). Typical plots of $\frac{1}{(I_o - I_t)}\left[\left(\frac{dI}{dt}\right)_t + \frac{k_e A}{V} I_t\right]$ vs. $\left[Q_t - \frac{V}{A k_e}(I_o - I_t)\right]$ for two particle sizes of Coal Valley coal yield two slopes (i.e., two rate constants, $k_{c,1}$ and $k_{c,2}$, respectively), indicating that the mechanism of coal oxidation changes with time of electrolysis, as in sulfuric acid. The rate constants are tabulated in Table 2, for the coals studied, along with selected properties of coal.

Table 2 shows that the sequence of the electrochemical activity of the coals is parallel to their fixed carbon (FC) content, as seen in the case of $H_2SO_4$ slurries [14,15] and that the rate constants are all higher in the acetic acid medium. It should be noted that a considerable degree of deviation from straight-line behavior in the kinetic plots were observed in all experiments in the short-time range (0-1 hr) of electrolysis. This is probably an indication of the presence of a wide variety of functional groups on the coal particle surfaces at early times of oxidation.

At relatively long times of electrolysis, the majority of the sites on the coal surfaces are probably oxidized to a common type and hence the oxidation mechanism is the same for the regions of $k_{c,1}$ and $k_{c,2}$. This is supported further by the observed constant rate of $CO_2$ production over the time period of $k_{c,1}$ and $k_{c,2}$ in acidic slurries [14-17].

### 3.3.3. *Chemical Oxidation of Coal slurries*

The validity of the kinetic treatment discussed earlier has bee further tested by determining the rate constant of coal oxidation b $Fe^{3+}$, with coal samples which are already oxidized electrochemically.

In one experiment, the coal slurry after 26 hours of electrolysis in 10 M HOAc + 3 M $H_2SO_4$ was kept at open circuit potential conditions for several days. During this period, the $Fe^{3+}$ in the slurry reacts fully with the coal, as indicated by the absence $Fe^{3+}$ when tested voltammetrically at a

microelectrode. To this slurry, small aliquots of a concentrated solution of ferric ammonium sulfate was added such that the final concentration of $Fe^{3+}$ would be 5 mM. The decrease in the concentration of $Fe^{3+}$ was measured as a function of time by applying a potential of 0.3 V vs RHE at a microelectrode (area = $1.9 \times 10^{-3}$ $cm^2$) and measuring the current with time. The microelectrode was used in order to limit the contribution of electrolysis at the electrode to a minimum. The I/t response was analyzed to obtain the rate constant of coal oxidation, since the rate of decrease of current is proportional to the rate of decrease of the $Fe^{3+}$ concentration as in equation (17).

$$\left[\frac{dI}{dt}\right]_t = - nFAke \left[\frac{dCo}{dt}\right]_t \qquad (17)$$

From equation (1), the rate of coal oxidation can be expressed as,

$$\text{Rate} = - \left[\frac{dCo}{dt}\right]_t = k_C \, C_{coal,t} \, Co_t \qquad (18)$$

Since only very small amounts of $Fe^{3+}$ are added to the slurry, the changes in the concentration of coal is negligible and hence, $C_{coal}$ is assumed to be constant throughout one addition experiment. Also,

$$Co_t = \frac{1}{nFAke} I_t \qquad (19)$$

and substituting equation (19) into (18),

$$- \frac{1}{nFAke} \left[\frac{dI}{dt}\right]_t = - k_C \, C_{coal} \, \frac{1}{nFAke} I_t \qquad (20)$$

$$\text{i.e. } \left[\frac{dI}{dt}\right]_t = k_C \, C_{coal} \, I_t \qquad (21)$$

Therefore, a plot of $\left[\frac{dI}{dt}\right]_t$ vs. $I_t$ should yield a straight line having a slope equal to $k_C \, C_{coal}$; the rate constant can then be

obtained by substituting in for $C_{coal}$, available from the x-intercept of the second slope of the kinetic plots.

The I/t response, obtained at microelectrodes after the addition of 5 mM $Fe^{3+}$ to a slurry of 6 grams of Coal Valley coal (200 mesh) which was electrolysed for 26 hours in 10 M HOAC + 3 M $H_2SO_4$ and maintained at OCP conditions, was analyzed using equation (21) to obtain the rate constant. A rate constant of 38 x $10^{-3}$ l $(mol.s)^{-1}$ was obtained by substituting $C_{coal}$ appropriately. This value is in close agreement with the rate constant, $k_{c,2}$ (Table 2), obtained using equation (16), thereby showing the validity of the kinetic treatment discussed earlier.

### 3.3.4 Product Analysis

#### 3.3.4.1 Gaseous Products

The gaseous products evolved from the anodic compartment containing 10M HOAc + 3M $H_2SO_4$ (in the presence of 15 mM $Fe^{2+}$) were analyzed at regular intervals throughout the electrolysis runs using GC. As in the case of $H_2SO_4$ slurries, $CO_2$ was the only gaseous product obtained in detectable quantities. The rate of production of $CO_2$ with time of electrolysis in the acetic acid slurry attained a steady-stae within a few hours of electrolysis. In Table 3, the cumulative charge efficiency (CE) for the production of $CO_2$ for 26 hours of electrolysis is tabulated for all of the coals. This term is an indication of the amount of non-gaseous products generated in the electrolysis experiment. As the CE decreases, the extent of coal liquefaction is likely to be

increasing.

The CE for the production of $CO_2$ from this mixed acid slurry as a function of the electrolysis time was determined by assuming that four electrons are involved in the production of one molecule of $CO_2$ from one carbon center having an oxidation state of zero. The efficiencies of $CO_2$ production shown in Table 3 are considerably lower than those obtained in sulfuric acid slurries [14,15]. These low $CO_2$ yields, together with the continuing high levels of electrochemical activity of the coal at long times of oxidation, are indicative of the continuous dissolution of oxidized surface moieties into solution with time of oxidation. This prevents the loss of active surface area with time, resulting in higher rate constants. Also, higher levels of dissolved liquid products are expected.

The results obtained in these acetic acid slurries indicate that the sequence of coal activity is Coal Valley > Bow City > Vesta > Highvale. Also, studies of 200 mesh coals vs. 60 mesh show that the smaller the particles (200 mesh), the more active the coal, consistent with their higher surface to volume ratios.

### 3.3.4.2 Liquid Products

The analysis of the dissolved products obtained from these experiments proved to be difficult, primarily because of the problems encountered in both the extraction step and in slow sample throughput in the chromatographic step, due to equipment failures and shortage of technical personnel over the course of

this research project. Also, it soon became apparent that each experiment would have to be repeated several times in order to be assured of the validity of the result for each set of conditions. As the electrolysis experiment, extraction and LC/MS analysis required more than one week of time per sample, this could not be done, particularly as the original plan to have all of the samples analyzed at the Alberta Research Council was abandoned, due to the high charges levied by them.

Even so, virtually all of the solutions used in the electrolysis of the various Alberta coals in the acetic/sulfuric acid slurry media underwent an extraction process and a liquid chromatogram was obtained for them. However, only in a few cases was there sufficient time and expertise available to analyze the peaks, either qualitatively or quantitatively, via on-line mass spectroscopy.

Figure 8 shows the LC obtained for the extractant from the cell in which 200 mesh Highvale coal had been electrolyzed in 10M HOAc + 3M $H_2SO_4$ (+ 15 mM $FeSO_4$) for 24 hours. It is clear that many liquid products have been obtained, with molecular weights primarily in the range of 168 and less, and with minor products having weights of 345 and 358. The primary products included $C_8H_{18}O_2$ (a saturated dihydric alcohol containing an isopropyl group), n-heptanol, n-butanol, $C_4H_8O_2$ (carboxylic acid), i.e. relatively low molecular weight oxygen-containing species, primarily alcohols and carboxylic acids, consistent with the polarity of the solution.

In comparison, the products obtained from Coal Valley coal, electrolyzed under almost identical conditions, appeared to be formed at a lower yield, but to have molecular weights more on the lower end of the scale. No other real conclusions can be drawn from the LC data obtained for the other coals electrolyzed in this medium

### 3.4 Electrochemical Oxidation of Coal in New Organic Acids

The possibility of the electrochemical oxidation of Alberta coals in various organic acids other than acetic acid and the extent of coal liquefaction achieved was tested using 60 mesh Coal Valley coal, due to the reproducibility of the results obtained with this particular sample in our earlier research. In most of these experiments, $Fe^{3+}$ was used as the mediator and the electrolysis was carried out at 90°C. The pH of the solution was adjusted to zero by adding sulfuric acid in order to facilitate the production of hydrogen, to stabilize the mediator in solution, and to suppress the ionization of the organic acids, thereby increasing the hydrocarbon solubilizing properties of the solution.

To the best of our knowledge, the electrochemical behavior of the $Fe^{2+/3+}$ mediator has not been reported previously in the literature for the organic media investigated in this work. Therefore, a detailed study of the suitability of the mediator for coal oxidation in these solutions was undertaken. It is known that the formal redox potential of the mediator depends

strongly on the nature of the solution and hence a knowledge of this potential was first sought. Also, the kinetic reversibility of the redox couple, as seen by the anodic to cathodic peak separation in a cyclic voltammetric experiment, as well as the electrochemical stability of the solution itself in the requisite potential range, was examined. For a reversible one-electron system, the peak separation should approach 60 mV. Of the solutions listed in Table 4, p-toluene sulfonic acid (PTA) provides the best conditions as far as the reversibility of the redox mediator is concerned, while oxalic acid was found to be unstable electrochemically when combined with sulfuric acid, similar to the known problems of using formic acid in such an experiment.

With the four organic acids which were ultimately studied, i.e., lactic acid, propionic acid, p-TSA and TFSA, i/t responses which either slowly or more rapidly decreased with time of electrolysis, were always observed. In the case of TFSA, the solvent was found to be highly dissociated and therefore very polar, with the result that the yield of liquid organic products was low and that of $CO_2$ was generally high. Of the other three, propionic acid, which is generally similar to acetic acid in terms of its properties, was found to yield the most promising results, exhibiting the lowest rate of production of gases, and a very high yield of liquid products (Table 5). This was seen both by the rich LC obtained for the extracted solution, as well as the very active i/t data obtained, even after over 24 hours of electrolysis. Therefore, it appears quite certain that Coal Valley coal

is readily converted to liquid products, with low yields of $CO_2$ and of surface-bound oxidized moieties, at the relatively low cell voltage of 1.0 V, with concurrent hydrogen production.

### 3.5 Electrochemical oxidation of coal in neutral organic solvents

Initial experiments were carried out with 60 mesh Coal Valley coal in a 10M DMSO + 3M $H_2SO_4$ slurry (Table 5). The redox potential of the $Fe^{2+/3+}$ mediator is ca. 0.4 V vs. RHE in this medium and therefore, coal electrolysis was carried out at ca. 0.8 V vs. RHE, i.e. at a voltage ca. 0.3 V less than employed in aqueous acidic slurries. DMSO is known to be a good solvent for many purposes and therefore, it was anticipated that a significant extent of coal liquefaction would be observed.

As expected, the electrochemical activity, seen in the routine i/t response, remained very high over a typical 24 hour electrolysis experiment. This is again indicative of the coal surface remaining relatively free of blocking oxidized compounds, and is correlated with the low $CO_2$ yields obsrved. This is also consistent with the rich chromatographic data obtained from the analysis of the solution. Unfortunately, neither a qualitative nor quantitative analysis of the liquid products could be obtained, due to the equipment and time constraints discussed in section 3.3.

Coal Valley coal was also oxidized in acetonitrile/3M sulfuric acid and THF/3M sulfuric acid slurries. Although the elec-

trochemistry of the mediator appeared to be very good in these solutions, and all early indications were that these solvents would be ideal for coal oxidation, it appears that these mixtures are unstable with time at 90° C, and therefore, further experiments in these environments were not carried out.

### 3.6 Coal oxidation in alkaline solutions

Two electrochemical mediators have been found which appear to be suitable in terms of solubility, electrochemical reversibility and redox potential in alkaline solutions. Initial trials focussed on $Ir^{3+/2+}$; however, it was found that after some time at 90°C, particularly if the potential exceeded 1.4 V vs. RHE, Ir metal/salts precipate, and hence further experiments could not be continued with this mediator.

A very promising mediator, $Co^{2+/3}$ as a bipyridyl complex, was reported in early 1989 [23]. Coal Valley coal was oxidized in a pH 11.5 slurry, using this Co complex as the mediator. The initial results appear to be very promising, with high levels of activity being exhibited even after long times of electrolysis, and very low yields of $CO_2$ obtained. Once again, conclusive statements regarding the types of liquid products obtained, and their yields, cannot unfortunately be provided.

## 4.0 ACKNOWLEDGEMENTS

This research was partially funded by a grant-in-aid of research from the Alberta/Canada Energy Resources Research Fund, jointly established by the Government of Canada and the Government of Alberta and administered by the Alberta Office of Coal Research and Technology. Scientific collaboration with Dr. G. Thomas was appreciated, and technical assistance from M. Chettiar, M. Farebrother, L. Malek, S. Whitcombe and R. Yamdagni is gratefully acknowledged. I am also grateful for financial assistance from the Natural Sciences and Engineering Research Council for the salaries of M.F. and S.W.

## REFERENCES


1. R.W. Coughlin and M. Farooque, Nature, **279**, 301 (1979).

2. M. Farooque and R.W. Coughlin, Nature, **280**, 666 (1979).

3. M. Farooque and R.W. Coughlin, Fuel, **58**, 705 (1979).

4. R.W. Coughlin and M. Farooque, J. Appl. Electrochem., **10**, 729 (1980).

5. G. Okada, V. Guruswamy, and J.O'M. Bockris, J. Electrochem. Soc., **128**, 2097 (1981).

6. R.P Baldwin, K.T. Jones, J.T. Joseph, and J.L. Wong, Fuel, **60**, 739 (1981).

7. P.M. Dhooge, D.E. Stilwell, and S.M. Park, J. Electrochem. Soc., **129**, 1719 (1982).

8. P.M. Dhooge and S.M. Park, J. Electrochem. Soc., **130**, 1029 (1983).

9. K.E. Anthony and H.G. Linge, J. Electrochem. Soc., **130**, 2217 (1983).

10. P.M. Dhooge and S.M. Park, J. Electrochem. Soc., **130**, 1539 (1983).

11. G. Kreysa and W. Kochanek, J. Electrochem. Soc., **132**, 2084 (1985).

12. O.J. Murphy, J.O'M. Bockris, and D.W. Later, Int. J. Hydrogen Energy, **10**, 453 (1985).

13. K.E. Johnson and L. Verdet, Can. J. Chem., **64**, 419 (1986).

14. V.I. Birss, George Thomas, and M. Chettiar, "Electrolysis of Alberta Coal Slurries", Final Report, Report No. 2835-RG-85/9, Alberta Office of Coal Research and Technology, Edmonton, Alberta, Canada (1988).

15. George Thomas, M. Chettiar, and V.I. Birss, (submitted to J. Appl. Electrochem.)

16. George Thomas, M. Chettiar, and V.I. Birss, (submitted to J. Electrochem. Soc.).

17. George Thomas, S. Whitcombe, M.D. Farebrother, and V.I. Birss, (submitted to J. Electrochem. Soc.)

18. George Thomas, M. Chettiar, and V.I. Birss, (to be submitted to J. Electrochem. Soc.).

19. Discussion between H. Linge and P.M. Dhooge et al concerning the

mechanism of electrochemical coal oxidation, J. Electrochem. Soc., **131**, 3023 (1984).

20. K.Kawakami, T. Okumura, K. Kusunoki, K. Kusakabe, S. Morooka, and Y. Kato, J. Chem. Eng. Jpn., **19**, 134 (1986).

21. S.B. Lalvani, Chem. Eng. Commun., **48**, 117 (1986).

22. A.J. Bard and L.R. Faulkner, in "Electrochemical Methods", John Wiley & Sons, New York, N.Y., Chapters 8,10,11 (1980).

Table 1. Origin, Rank and Particle Sizes of Alberta Coals

| Sample Type[a] | Geological Formation | ASTM Rank[b] | Particle Size | |
|---|---|---|---|---|
| | | | mesh | µm |
| Luscar-Sterco Coal Valley | Mynheer/Valdor | hvB C | >200 | <65 |
| " | " | " | 48 - 64 | 250 - 350 |
| Highvale | Paskapoo | Sb B | >200 | <65 |
| " | " | " | 48 - 64 | 250 - 350 |
| Antelope-Bow City (Brooks) | Oldman | Sb B | >200 | <65 |
| " | " | " | 48 - 64 | 250 - 350 |
| Vesta (Central Battle River) | Horseshoe/Canyon | Sb C | >200 | <65 |
| " | " | " | 48 - 64 | 250 - 350 |

[a]Samples collected from Alberta Plains Coal Region; [b]Sb = Sub-bituminous, hvB = high volatile bituminous.

**Table 2**

Electrochemical Rate Constants* for the Oxidation of Alberta Coals by $Fe^{3+}$ in 10M HOAc + 3M $H_2SO_4$

| Coal | 200 mesh | | 60 mesh | |
|---|---|---|---|---|
| | $k_{c,1}$ | $k_{c,2}$ | $k_{c,1}$ | $k_{c,2}$ |
| Coal Valley | 682 | 156 | 214 | 27 |
| Highvale | 112 | 30 | 134 | 22 |
| Vesta | 115 | 32 | 112 | 21 |
| Bow City | 71 | 18 | 93 | 17 |

* all rate constants x $10^3$ litre $mol^{-1}s^{-1}$; all experiments carried out at 1.0 V vs. RHE at 90° C.

**Table 3**

Carbon dioxide collection data for electrochemical oxidation of Alberta coals in 10M HOAc + 3M $H_2SO_4$ *

| Coal | Particle size (mesh) | Total Charge (C) | $CO_2$ rate (cc/hr) | Total Volume $CO_2$ (cc) | CE % |
|---|---|---|---|---|---|
| Coal Valley | 60 | 1581 | 0.15 | 3.9 | 4.2 |
| | 200 | 2490 | 0.45 | 11.7 | 8 |
| Highvale | 60 | 1828 | 0.47 | 12.3 | 11.5 |
| | 200 | 2282 | 1.4 | 33.6 | 25 |
| Vesta | 60 | 1970 | 0.7 | 18.2 | 16 |
| | 200 | 2260 | 0.75 | 19.5 | 15 |
| Bow City | 60 | 1190 | 0.4 | 10.4 | 15 |
| | 200 | 2349 | 1.2 | 28.8 | 21 |

* all electrolysis experiments carried out for 24 to 26 hours, at 1.0 V vs. RHE, at 90° C.

**Table 4**

Electrochemical Data for oxidation/reduction of $Fe^{2+/3+}$ in various organic-based environments at 25°C

| Medium | pH | s (mV/s) | $\Delta E_p$ (mV) | $E^{o'}$ (V vs. SHE) |
|---|---|---|---|---|
| 1:1 Lactic Acid + $H_2SO_4$ | 0.4 | 20 | 0.11 | 0.675 |
| | | 50 | 0.14 | 0.685 |
| | | 100 | 0.16 | 0.682 |
| | | 200 | 0.20 | 0.680 |
| 1:1 PTSA + $H_2SO_4$ | 0.2 | 20 | 0.08 | 0.700 |
| | | 50 | 0.085 | 0.692 |
| | | 100 | 0.09 | 0.685 |
| | | 200 | 0.09 | 0.65 |
| 1:1 Citric Acid + $H_2SO_4$ | 0.5 | 20 | 0.145 | 0.692 |
| | | 50 | 0.180 | 0.690 |
| | | 100 | 0.220 | 0.700 |
| 1:1 Tartaric Acid + $H_2SO_4$ | 0.4 | 20 | 0.200 | 0.700 |
| | | 50 | 0.260 | 0.700 |
| | | 100 | 0.310 | 0.705 |
| | | 200 | 0.330 | 0.695 |
| 1:1 Proprionic Acid + $H_2SO_4$ | 0.5 | 20 | 0.150 | 0.675 |
| 0.5 M $CF_3COOH$ | 0.61 | 20 | 0.080 | 0.750 |
| | | 100 | 0.100 | 0.750 |
| 10M $CH_3CN$ + 1M $H_2SO_4$ | 0.45 | 10 | 0.120 | 0.700 |
| | | 20 | 0.100 | 0.700 |
| | | 100 | 0.170 | 0.685 |
| | | 200 | 0.240 | 0.700 |
| 10M DMSO + 1M $H_2SO_4$ | 0.4 | 20 | 0.060 | 0.440 |
| | | 50 | 0.075 | 0.437 |
| | | 100 | 0.080 | 0.440 |
| | | 200 | 0.080 | 0.440 |
| 1:1 THF + $H_2SO_4$ | 1.1 | 20 | 0.120 | 0.660 |
| | | 50 | 0.130 | 0.655 |
| | | 100 | 0.180 | 0.660 |
| | | 200 | 0.250 | 0.655 |

**Table 5**

$CO_2$ Collection Data for Electrochemical Oxidation of Coal in New Environments *

| Medium | Total Charge (C) | $CO_2$ Rate (cc/hr) | $CO_2$ Volume (cc) | CE % |
|---|---|---|---|---|
| 5M Lactic Acid + 3M $H_2SO_4$ | 1010 | 0.2 | 5.2 | 9 |
| PTSA (3M) + 3M $H_2SO_4$ | 1086 | 0.19 | 4.8 | 7.6 |
| 5M Propionic Acid + 3M $H_2SO_4$ | 1523 | 0.15 | 4.0 | 4.5 |
| 10M DMSO + 3M $H_2SO_4$ | 510 | 0.09 | 2.3 | 8 |

* 6 grams of 60 mesh Coal Valley coal, 90°C

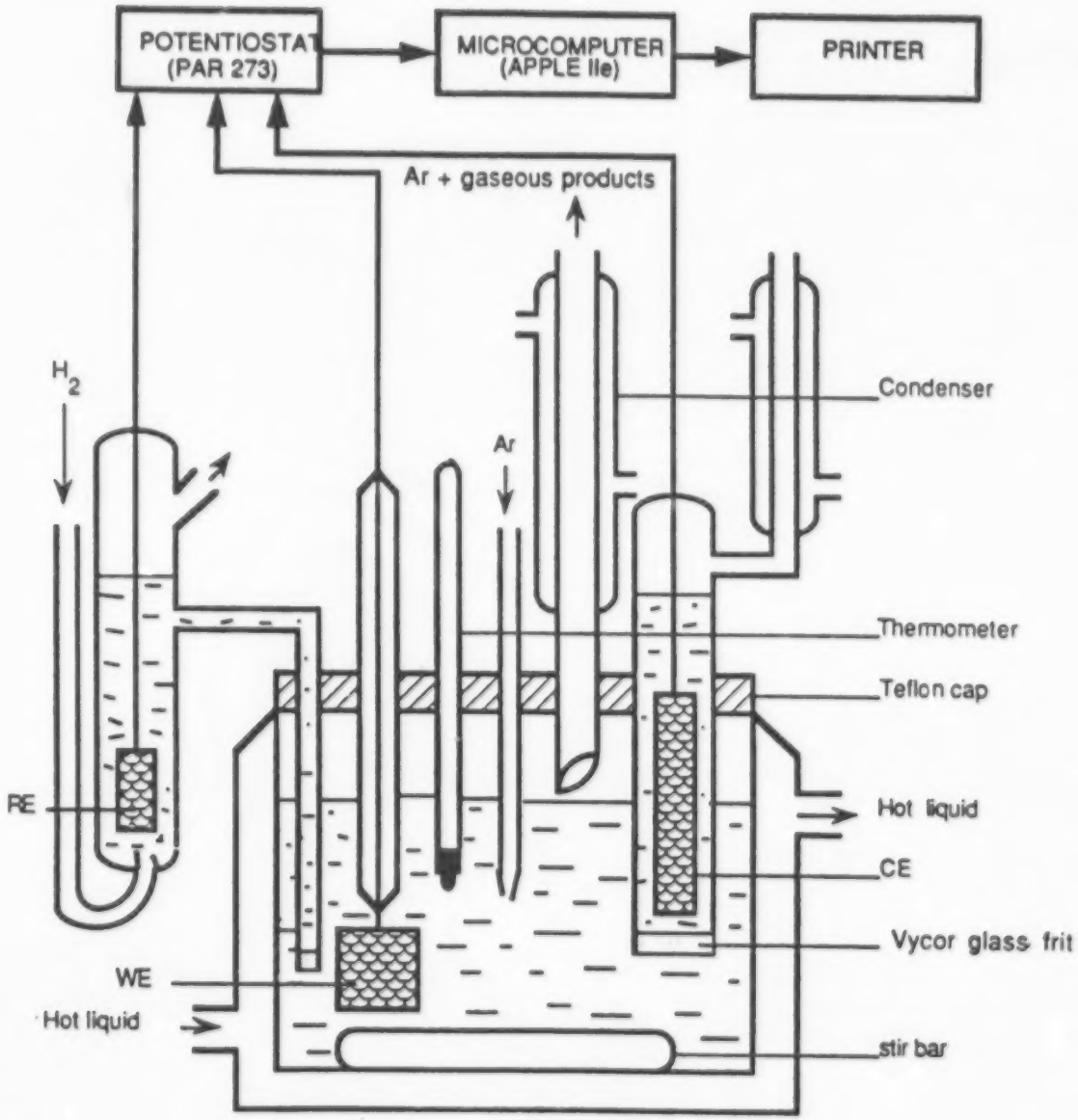


FIG. 1 Electrochemical cell and instrumental set-up

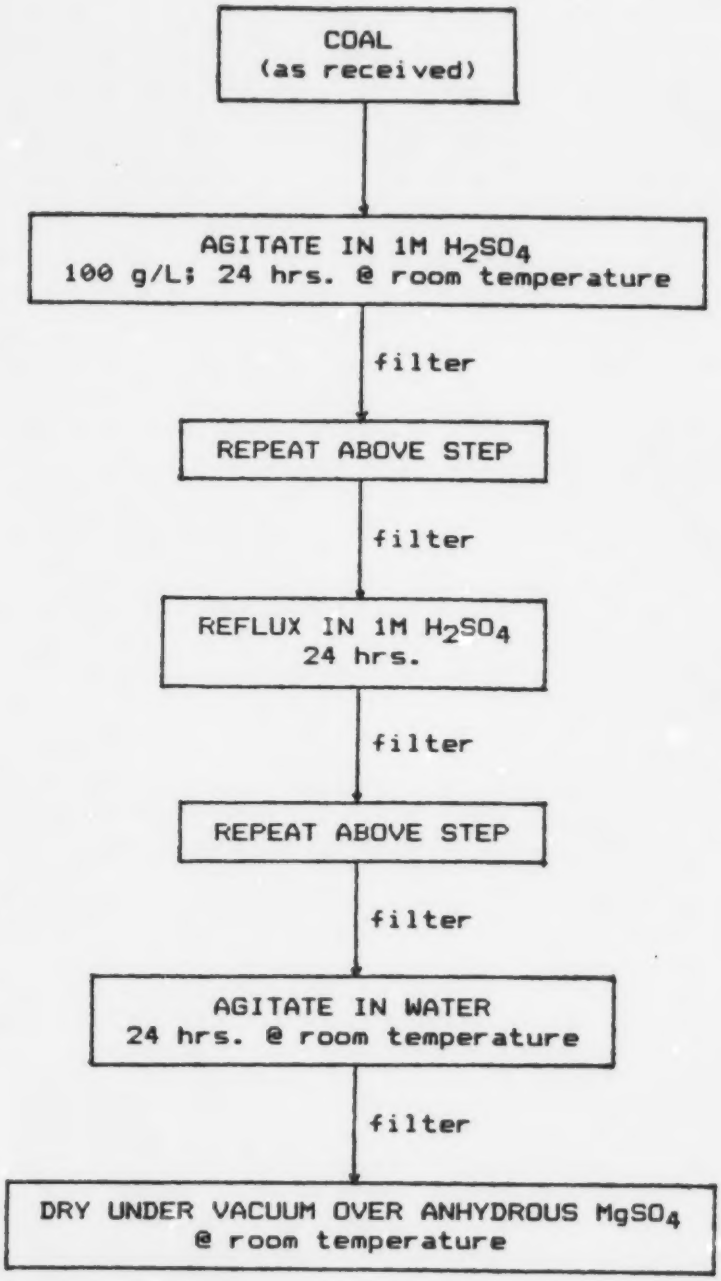


Fig. 2 Sequence of steps followed during coal pretreatment process.

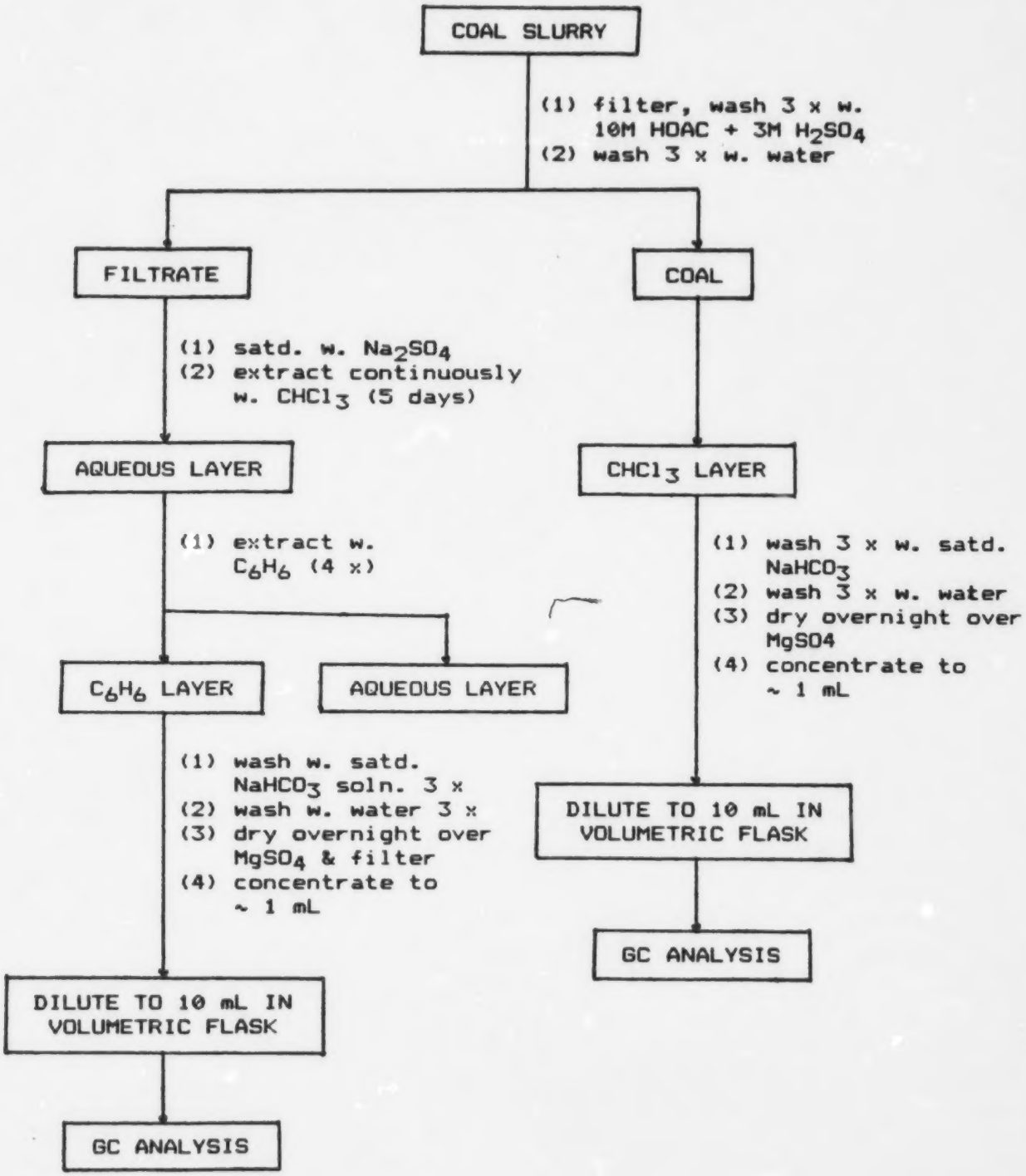
COAL SLURRY
(1) filter, wash 3 x w. 10M HOAC + 3M $H_2SO_4$
(2) wash 3 x w. water
FILTRATE
COAL
(1) satd. w. $Na_2SO_4$
(2) extract continuously w. $CHCl_3$ (5 days)
AQUEOUS LAYER
$CHCl_3$ LAYER
(1) extract w. $C_6H_6$ (4 x)
(1) wash 3 x w. satd. $NaHCO_3$
(2) wash 3 x w. water
(3) dry overnight over MgSO4
(4) concentrate to ~ 1 mL
$C_6H_6$ LAYER
AQUEOUS LAYER
(1) wash w. satd. $NaHCO_3$ soln. 3 x
(2) wash w. water 3 x
(3) dry overnight over $MgSO_4$ & filter
(4) concentrate to ~ 1 mL
DILUTE TO 10 mL IN VOLUMETRIC FLASK
GC ANALYSIS
DILUTE TO 10 mL IN VOLUMETRIC FLASK
GC ANALYSIS

FIG. 3 Liquid-liquid extraction process used with 10 M acetic acid + 3 M sulfuric acid slurries.

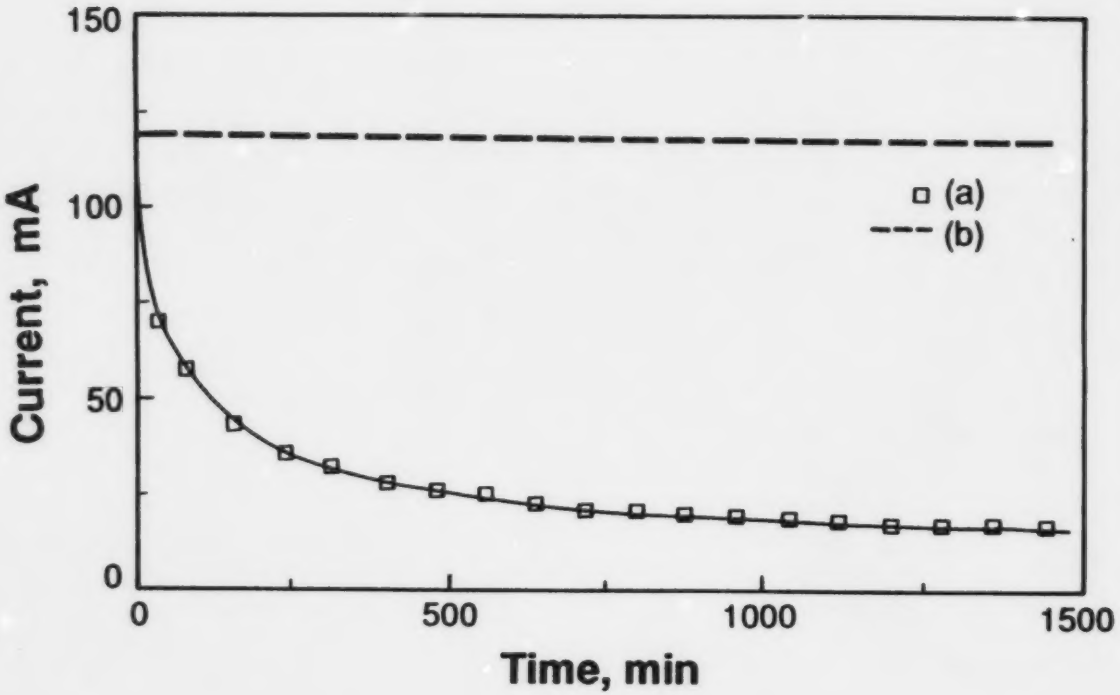


FIG. 4 i/t transiet obtained during electrolysis of 6 gms Vesta coal in 1M $H_2SO_4$ (+ 15 mM $Fe^{2+}$) at 90°C (curve a), compared to hypothetical response (curve b) if $Fe^{2+}$ were completely regenerated.

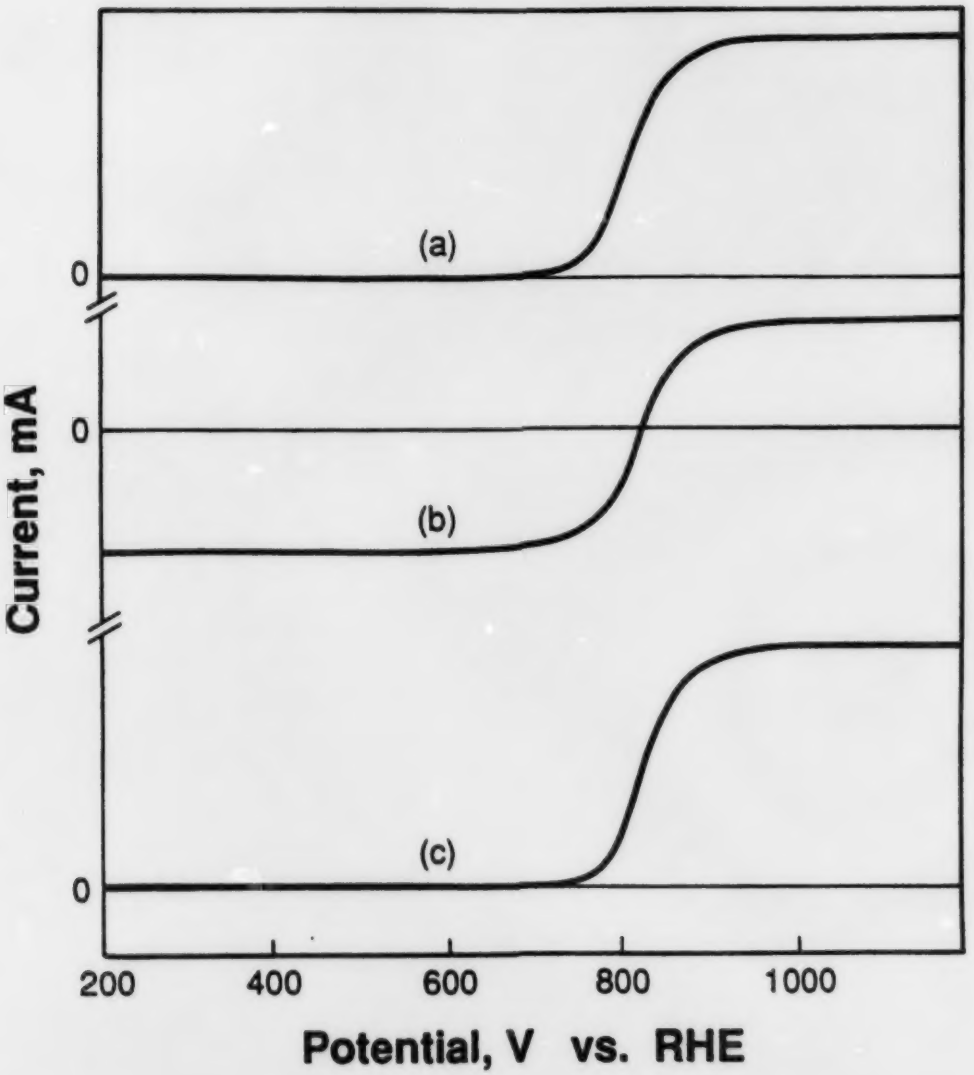


FIG. 5 Schematic plots of CV response before (a), during (b) and at completion (c) of coal slurry electrolysis experiments.

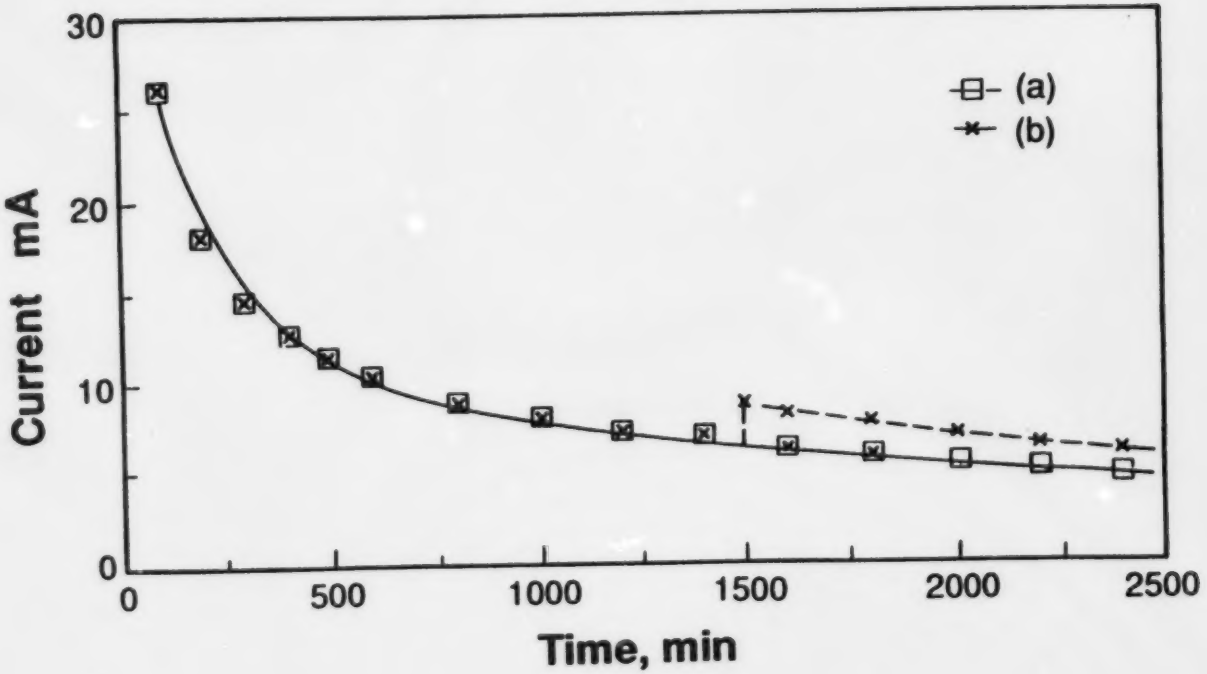


FIG. 6 Effect (curve b) of addition of small aliquot of $Fe^{2+}$ to substantially oxidized coal slurry after ca. 24 hrs. (curve a) of electrolysis.

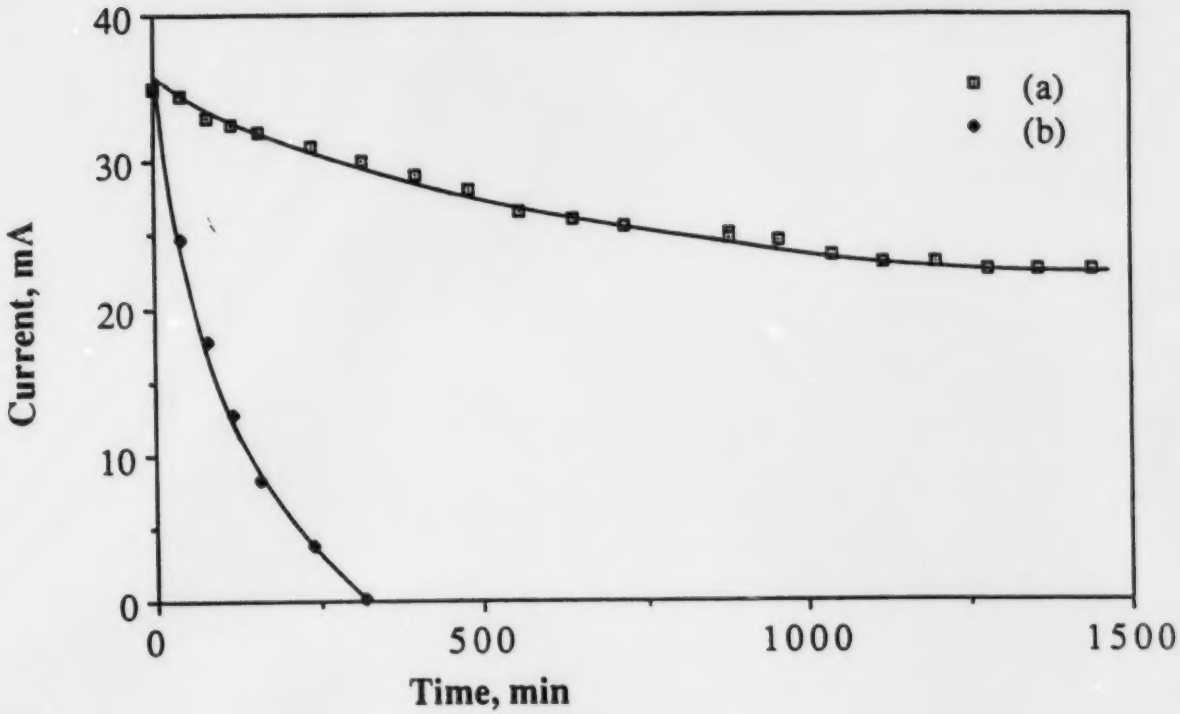


FIG. 7 I/t response obtained in 10 M acetic acid + 3 M $H_2SO_4$ during the oxidation of (a) 6 grams of Vesta coal (200 mesh) + 15 mM $FeSO_4$, and (b) 15 mM $FeSO_4$ (no coal).

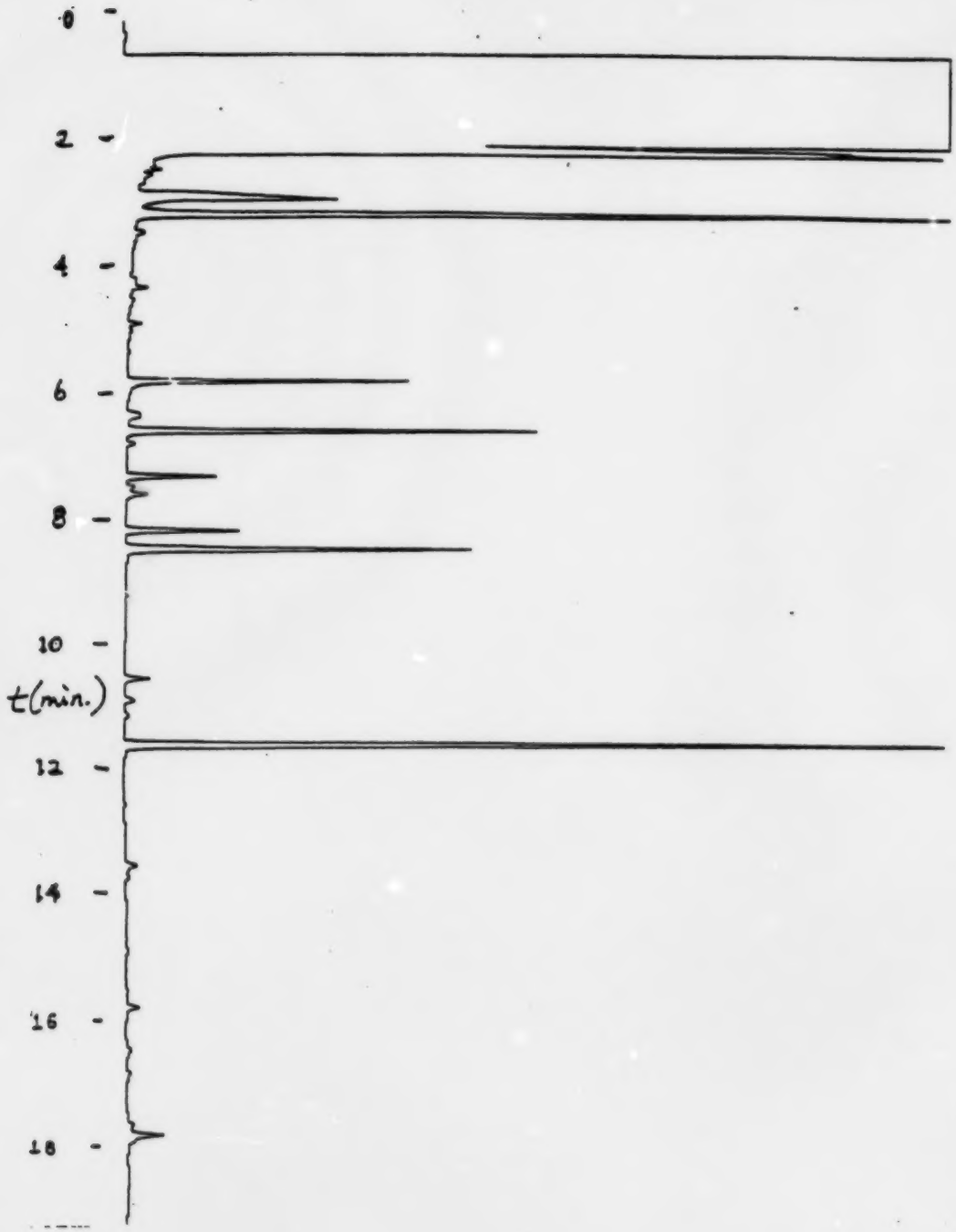


FIG. 8 Liquid chromatogram obtained for solution extracted from experiment in which 200 mesh Highvale coal was electrolyzed in 10M HOAc + 3M $H_2SO_4$ for 24 hrs at 90°C.